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The Stability of Organometallic Compounds During Their Synthesis and Decomposition

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Various aspects of the stability of organometallic compounds on the basis of the concept of the stability and structure of material systems are considered. The energy and steric factors in stability are discussed.
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I. INTRODUCTION

The problem of the stability of organometallic compounds (OMC) arose during the dawn of the development of organometallic chemistry as a specific problem in the synthesis of OMC of non-transition[1] and transition[2] metals. A large number of thermally stable organoelemental compounds have been obtained with non-transition metals and non-metals. As regards transition metals, stable compounds have been obtained only in studies on the synthesis of polyaryl derivatives of chromium,[3] molybdenum,[4] and tungsten.[5] However, owing to the difficulty of the synthesis, further studies on these compounds were not performed up to 1954–1955. During these years polyphenylchromium compounds were again synthesised, their reductive decomposition was investigated, and their sandwich structure was confirmed.[6]

During the 1940s–1950s, the view arose that fully alkylated OMC of *d* and *f* elements are unstable and involatile on the basis of Nesmeyanov's,[7] Cotton's,[2] and Jaffé's[8] generalisations (the Mendeleev–Grosse–Nesmeyanov rule). Since the discovery[9] of biscyclopentadienyliron Cp_2Fe, having the sandwich structure, aromatic character, and a high stability (thermal, oxidative, etc.) the problem of the stability of OMC, particularly those of transition metals, has undergone a new development. Stable and volatile OMC of transition metals with many-centre bonds, the so-called polyhapto-(η^n)-derivatives of π-electron ligands and metals were synthesised.

At approximately the same time, Chatt's concept[10] of the stability of transition metal OMC containing a two-centre two-electron σ-bond with an alkyl or aryl ligand and having an electron shell of the next inert gas in Mendeleev's Table, built up by the electrons of electron-donating ligands (phosphines, etc.), was published. These views were confirmed by a series of experimental studies designed to synthesise σ-derivatives of platinum, palladium, and other metals.[11] Somewhat later, after the publication of the communications by Ziegler and Natta on the catalysis of the polymerisation of olefins,[12] experimental studies on the synthesis of alkyl (methyl, ethyl, etc.) derivatives of transition metals (titanium, chromium, manganese, etc.[11]) were published. Various investigators explained the low thermal stabilities of these compounds either in terms of thermodynamic or kinetic instability.

In their investigations of the problem of the kinetic stabilisation of σ-derivatives of transition metals, Wilkinson,[13] and Lappert and co-workers[14] achieved considerable successes in the synthesis of thermally stable OMC using bulky sterically hindered alkyl groups without C–H bonds in the β-position (in order to prevent the olefin-hydride decomposition of the OMC).

The problem of the stability of non-transition metal OMC has not arisen in quite such an acute form as for transition metals with the exception of the question of the stability of extravalence compounds, such as the pentacovalent derivatives of Group VA elements, and the question of the possibility of the olefin-hydride decomposition of OMC, for example, those of aluminium.

Studies on the radical decomposition *in vacuo* of lead, tin, and other metal alkyls,[15] on the photodecomposition in the gas phase of lead, mercury, and other metal alkyls,[16] and on the thermal reactions of alkyl and phenyl compounds of mercury, lead, tin in the condensed phase under hydrogen pressure in the presence and absence of catalysts, which have been described by Razuvaev,[17] may be regarded as some of the first investigations designed to determine the stability of non-transition metal OMC not as regards the possibility of their synthesis in principle but as regards the pathways and ease of decomposition of the OMC. Subsequently these studies were extended to the thermal and photochemical reactions of non-transition metal OMC in solution[18] and their aim became the demonstration of the formation of free radicals and their involvement in the reactions.[19]

In recent years the problem of the stability of OMC in relation to various decomposition processes arose anew in connection with the practical employment of OMC—for the preparation in the course of their decomposition of inorganic coatings and materials,[20,21] for the preparation of gaseous metals from OMC as active substances in gas lasers,[22,23] and also in connection with the extensive possibilities of the new methods of synthesis of OMC (the direct synthesis of OMC by the cocondensation of metal vapours with organic compounds,[24,25] the electrochemical synthesis of OMC,[26] the

radiation-chemical synthesis of OMC,[27] the plasma-chemical synthesis[28] and decomposition[29] of OMC in the gas phase). The application of these methods is frequently complicated by the instability of the OMC under the conditions of their synthesis or use, which gives rise to the necessity for the determination of the stability of OMC in various processes and under various conditions.

In the chemical literature there is no single combined approach to the problem of the stability of OMC. The authors only partially discussed the thermodynamic or kinetic aspect, the quantum-chemical aspect of the stability of OMC was considered in isolation from the former, and there have been virtually no studies on the stability of OMC under real non-equilibrium conditions in the presence of mass and energy fluxes. The aim of the present review is to consider critically, from a single standpoint, the concept of the stability of an isolated OMC molecule and also of systems incorporating OMC and their decomposition products in various states of aggregation, the energy and steric factors in the stability of OMC, and their manifestations under various conditions. Different aspects of the stability of OMC in the OMC synthetic and decomposition processes occurring under the following conditions are considered: thermal reactions involving uncharged (neutral) OMC species and the decomposition products; electron impact under the influence of an electric current with participation of charged (ionised) species; the effect of electromagnetic radiation with different energies and intensities (including laser radiation).

1. The Concept of the Stability of OMC

The concept of the stability of the state of a material system in time and space is fundamental. Its essential feature for a system of atoms or molecules having a definite order in space is the ability of the system to exist, subject to the influence of internal and external forces, in an equilibrium which corresponds to a definite energy level and their ability to return to a state of equilibrium after any kind of perturbation. The stability of the system in relation to various perturbations is almost always different and depends on the nature and character of the perturbations. When the latter is not specified, the stability of the system in relation to any perturbations is implied.

The set of stable bonds in a system of atoms and molecules ensuring the integrity and identity of the system itself in space and in time, constitutes the concept of the structure of the system. Hence the stability of the structure of a system is a characteristic of the stability of the system as a whole.

The stability of the structure of OMC is determined by two factors—energy and steric factors. The state of the system, for example an OMC molecule, is described by the solution of the Schroedinger equation, in which the eigenvalues of the energy (the energy factor) and the coordinate-temporal wave eigenfunctions (the steric factor) play equivalent roles. The eigenvalues of the energy and the steric localisation—delocalisation of the wave functions of the molecule can help to explain the energy and steric-specific features of the stability of OMC (for stationary time-independent solutions). Accordingly, in the analysis of the stability of OMC it is useful to consider in succession the energy and steric OMC stability factors in relation to various types of perturbations of the system or in relation to various types of OMC synthetic and decomposition reactions, in particular, the relation between the structure of OMC (the molecular structure, the structure of the condensed state) and stability and its influence on the reaction mechanism.

It is possible to differentiate four general aspects of the study of the stability of OMC, covering the molecular and electronic structures of OMC, all possible states of aggregation of OMC, their dynamics, and their interaction with fluxes (energy and mass fluxes): (1) the stability of an isolated OMC molecule (quantum-chemical stability); (2) the stability of systems incorporating OMC and their decomposition products in definite states of aggregation and at equilibrium (thermodynamic stability); (3) the dynamic stability of thermodynamically reversible systems incorporating OMC and their decomposition products in definite states of aggregation at equilibrium and in the vicinity of equilibrium and the rate of approach to equilibrium by the system (kinetic stability); (4) dynamic stability of thermodynamically irreversible systems consisting of OMC and their decomposition products in definite states of aggregation in the presence of mass and energy fluxes both near and far from thermodynamic equilibrium (the formation and stability of dissipative structures, macrokinetic aspect).

The first two aspects refer to the description of systems having a time-independent spatial structure, while the second two characterise the stability of systems with a time-dependent spatial-temporal structure.

II. QUANTUM-CHEMICAL STABILITY

We shall consider the quantum-chemical stability of OMC, concentrating attention initially on the energy factor (the stability of the electronic structure of the OMC molecule) and on the steric factor (the stability of the molecular structure of the OMC) and also on the description of the possible states of OMC with the aid of potential energy surfaces, the description including both factors. In conclusion we shall discuss the main types of possible perturbations of the OMC molecule which determine its stability.

The main criterion of the possible existence of an isolated OMC molecule (*in vacuo*) is the quantum-chemical stability. A quantum-chemical estimation of the stability of the OMC molecule presupposes the consideration of electron shell stability (the electronic configuration, structure) of the molecule relative to the stability of the electron shells of isolated molecules (species) of the decomposition products considered in valence states. Overall, the quantum-chemical stability of OMC is determined,[30] firstly, by the electronic configuration (structure), of the OMC molecule, i.e. the distribution of electrons among the bonding, non-bonding, and antibonding MO; secondly, the binding energy in each MO, i.e. the decrease of the energy of the bonding MO relative to the energy of the constituent orbitals of the isolated fragments; thirdly, the non-bonding interactions (usually repulsive), which characterise the steric hindrance in the OMC molecule and determine its steric structure.

There exist a series of theoretical and empirical criteria of electron shell stability in OMC and their molecules, characterising their quantum-chemical stability. For the majority of ions of the elements in the Periodic System, metal carbonyls, and the OMC of non-transition and transition metals, there exists a rule which states that a closed electron shell is stable. For compounds having a central atom of an element, the most stable (closed) electron shell is that which attains the electronic structure of the shell of the next inert gas in Mendeleev's Table by employing electrons of all the ligands involved in the bonds with the element (the extension of Sidgwick's rule[31] to ions). The most stable compounds are formed precisely in conformity with the "inert gas rule" (for example, ferrocene, dibenzenechromium, virtually all the

transition metal carbonyls, especially mixed cyclopentadienyl- or arene-metal carbonyls, etc.), although there exist many exceptions to this rule. The inert gas rule is the overall consequence of Hund's rule,[32] which states that unoccupied, half-occupied, and wholly occupied subshells are stable (the *s*, *p*, *d*, and *f* shells).

In organic complexes of metals and in OMC molecules this stability criterion leads to the stabilisation of both low-spin and high-spin states, for example, in $(C_5H_5)_2Mn$ stabilisation of the configuration with maximum spin (five unpaired electrons) is energetically favourable, whereas in ferrocene as well as in the ferrocenium cation, which is isoelectronic with manganocene, stabilisation of the low spin configuration is observed.

A special case of the overall effect of the stabilisation of the electronic structures of derivatives of non-transition elements is the octet rule (involving the s^2p^6 electronic configuration).[30]

Mendeleev's remark, contained in the early editions of "Principles of Chemistry" (up to the eighth),[33] namely that only the elements in the odd series are capable of forming organometallic compounds and that, when an element forms a hydrogen compound EH_x, it also forms organometallic compounds ER_x, constitutes one of the first formulations of the OMC stability rules. Grosse[34] assumed that only the elements whose valence electrons are located in levels with the same principal quantum number, i.e. non-transition elements, give rise to typical alkyl compounds.

On the basis of a survey of extensive experimental data, Nesmeyanov[7] formulated the following rule: "alkyl groups are bound fairly stably to an element only via *sp*-valence levels. The presence in the atoms of even unused *d* or *f* valence electrons cause a sharp weakening of the stability of the resulting alkyl derivatives, renders them atypical and involatile, and altogether prevents their existence". In his generalisations,[7,35] Nesmeyanov discussed the thermal instability and stability of OMC, which he estimated either on the basis of the possibility of the existence of compounds at room temperature or at the decomposition temperature.

The Mendeleev–Grosse–Nesmeyanov rule has received a theoretical quantum-chemical justification in Jaffé's studies.[8] According to Jaffé, the M–C σ-bonds are weaker for transition metals than for all the principal elements and their strength increases with increasing *s* character of the hybrid carbon orbitals of the group linked to the metal: sp^3 (alkyls) < sp^2 (aryls) < *sp* (acetylides). When aryl groups are bound to transition metals, there is a possibility of additional strengthening of the bond and there is also the formation of π-bonds, both donor–acceptor Ar → M bonds of the types $2p_\pi \rightarrow np_\pi$ and $2p_\pi \rightarrow (n-1)d_\pi$ (for transition metals) or $2p_\pi \rightarrow nd_\pi$ (for non-transition elements), and dative M → Ar bonds (via the pairs of electrons of the d_π orbitals of the metal). In the experimental studies of Chatt and co-workers[10] on the stability of organic derivatives of Group VIII metals it was established that the OMC is stable in relation to thermal dissociation when all the bonding MO are populated by pairs of electrons, for example, the electrons of phosphine, amine, or carbonyl ligands. In this case the carbon-transition metal σ-bond is stabilised and there is a possibility of isolating stable OMC, for example, $CH_3Mn(CO)_5$, $Alk_2Ni(PR_3)_2$, etc.

The OMC stability rules quoted above refer to the degree of population of the bonding, non-bonding, and anti-bonding MO. If all the bonding MO are populated by electron pairs and the non-bonding MO, if such exist, are not orbitals of the π-system but constitute the orbitals of unshared electron pairs of the ligand heteroatoms or the orbitals of the electrons in the metal atom which are non-bonding in relation to ligands, then such an electronic configuration (structure) of the OMC should be stable in the quantum-chemical aspect (analogously to Hückel's rule concerning the stability of aromatic systems). The stability of the electronic structure of OMC, expressed in terms of these theoretical and empirical rules, is based on the fact that, on formation of the entire system of chemical bonds in the molecule between the metal and the ligands, there is an overall energy decrease of all the electrons in the molecule relative to the isolated ligands and the metal atom. This decrease corresponds to the stabilisation of the electron shell both via the formation of chemical bonds and because the closed electron shell is favoured by energy factors.

The methods of ultraviolet, X-ray, and photoelectron (PES) spectroscopy[36] make it possible to determine experimentally the vertical and adiabatic ionisation potentials of the molecules and to find the sequence of energy levels of the electrons involved in the M–C, C–C, C–H, etc. bonds and also of the non-bonding electrons of the metals, which yields complete information about the energy distribution of the electrons in OMC. On the basis of experimental studies of mononuclear and polynuclear OMC of non-transition and transition metals,[37–39] the sequences of the energy levels of the electrons in OMC have been established. Under the conditions where Koopman's theorem is applicable, this yields an idea about the sequence of the energies of the one-electron molecular orbitals[40] and, when Koopman's theorem is inapplicable, it yields the sequence of the energies of the multielectron levels of the molecule.

The non-bonding electrons of the metal are usually located in the highest of the occupied MO and below these are the MO which correspond to the electrons involved in the metal–metal σ-bonds or the metal–ligand δ- and π-bonds. These are followed by the strong bonding MO corresponding to the metal–ligand (group) σ-bonds and the σ-bonds within the ligands (C–C and C–H).

Consideration of the OMC stepwise dissociation (decomposition) process shows that each reaction stage can be modelled by means of a two-particle approximation and, by analogy with diatomic molecules, one can assume that the dependence of the energy on the metal–ligand distance is described by a potential curve resembling the Morse curve. In this case one can speak of the dissociation energies of specific bonds (D_1, D_2, etc.) formed by the metal-containing fragment of the OMC molecule and the ligand:

$$R_nM \rightarrow R_{n-1}M \ldots R \xrightarrow{D_1} R_{n-1}M + R;$$
$$R_{n-1}M \rightarrow R_{n-2}M \ldots R \xrightarrow{D_2} R_{n-2}M + R \quad \text{etc.}$$

The quantities D_n are determined by mass-spectrometric or thermochemical methods. The average bond dissociation energies *D*, determined experimentally for the gas-phase total dissociation of the OMC, are used in many cases as a measure of the strength of the metal–ligand bond in the OMC:[41–43]

$$R_nM\ (\text{gas}) \overset{n\bar{D}}{\rightleftarrows} M\ (\text{gas}) + nR\ (\text{gas}). \qquad (1)$$

For the majority of the metals investigated, the values of D_n or *D* are always much greater than zero and usually amount to between 20 and 100 kcal mol^{-1} and more.[41–43] Consequently the formation of isolated OMC molecules is energetically favourable. On the other hand, the stability of the molecules produced depends on the stability of the electronic structure acquired by the metal in the OMC and on the stability of the steric molecular structure of the OMC.

Proceeding now to the consideration of the stability of the molecular structure of OMC, we may note that the latter depends on the spatial distribution of the electron density associated with the chemical bonds, the unshared electron

pairs, and the non-valence interactions between ligands which are not linked by bonds, i.e. on the steric factor. When the non-valence interactions do not give rise to steric hindrance to the formation of the molecular structure, the stability of the latter is determined by the extent to which the corresponding spatial distribution of electron density and the atomic nuclei is energetically favourable, this being determined by the structure of the electron shells of the OMC, the metal atom, and the ligands.

If the ligands form chemical bonds with the metal via one of their sp^3, sp^2, or sp orbitals, then the electronic structure of the OMC of non-transition and transition metals represents[44] a set of two-electron two-centre σ-bonds, one of which is localised on each ligand. The number of such bonds, their spatial distribution, and the stability of the OMC are determined by the structure of the electron shell of the metal, the number of valence electrons, and the number and type of unoccupied atomic orbitals (AO) of the metal. For ligands with sp^2 and sp valence orbitals, weak or strong π-bonds,[44] involved in p_π–p_π or p_π–d_π interactions, may be formed in addition to the σ-bonds. In order to find the most stable configurations of molecules of the type MR_n use is made of Pauling's[45] and Murrell's[46] maximum overlap method, which has been successfully developed by other workers.[47–49]

Organic ligands containing an unsaturated π-electron system (η^n-ligands: alkenes, alkynes, allyl, cyclobutadiene, cyclopentadiene and cyclopentadienyl, benzene, etc.) give rise to considerable possibilities for the formation of many-centre metal–ligand bonds in OMC molecules. Many-centre two-electron σ-, π-, and δ-bonds are usually formed along the principal symmetry axis of the ligand and in the case of transition metals such organic derivatives have a sandwich structure.[11]

The strength of the bonds between polyhapto-ligands and transition metal atoms is determined by the total number of two-electron many-centre bonds formed with the given ligand and reaches a maximum on formation of the maximum number of the possible bonds. With increase of the metal–ligand distance, the strength of the π- and especially δ-bonds diminishes sharply in contrast to the σ-bond, which acts over a longer range.[50]

The nature of the bonds between polyhapto-ligands and non-transition metals such as silicon, germanium, and tin is close to that of the analogous bonds with transition metals, i.e. also delocalised over the ligand,[51,52] although, by virtue of the lack of the ability of the electron shells of these metals to form many-centre π- and δ-bonds, they are comparatively weak σ-bonds.[51]

The stability of OMC containing bonds between polyhapto-ligands and transition metals is frequently strikingly high. Compounds in the molecules of which all the bonding MO are occupied by pairs of electrons (in many cases such filling of the MO corresponds to the inert gas rule) are especially stable.

The spatial distribution of the many-centre bonds in the OMC molecule depends, analogously to the two-centre σ-bonds, on the electronic structure of the metal and also on the presence or absence of steric hindrance owing to the repulsion of the non-bonded ligands (the effect of the latter is the steric and energetic non-equivalence of the ligands and of their bonds with the metal, for example, the existence of different numbers of η^5- and η^1-C_5H_5 ligands in compounds of the type $(C_5H_5)_4M$ (M = Ti, Zr, or Hf),[53] etc.

Overall, the delocalisation of electrons over many centres, which leads to the formation of a many-centre transition metal–ligand bond, increases significantly the stability of OMC. Stabilisation of labile metal–carbon bonds also results from the formation of a chelate ring via a neighbouring (usually in the β-position within the substituent group or in the *ortho*-position in a phenyl substituent) electron-donating group of the type of $\ddot{N}R_2$, $\ddot{O}R$, and $\ddot{P}R_2$.[54]

The next type of intramolecular interactions influencing the stability of OMC molecules are the so-called additional interactions, intermediate between valence (bonding) and non-valence (repulsive) interactions.[55] By binding the metal atom to the substituent group (ligand) or the ligands to one another, these interactions increase the quantum-chemical stability of the OMC, as happens, for example, in the case of $[(C_6F_5)_3Ge]_2Hg$.[56]

As already mentioned, the non-bonding interactions, namely the repulsions between the substituent groups (ligands) not linked by valence bonds, the unshared electron pairs, and atomic nuclei, play an important role in the formation of the molecular structure of the OMC and its stability. They can influence appreciably the extent of the bonding and additional interactions up to complete blocking of the possibility of bond formation. The non-bonding interactions in the OMC molecule lead, on the one hand, to the steric shielding of the metal atom (or a group of metal atoms in polynuclear OMC and metal clusters) by substituents (ligands) (this characteristic of the OMC molecule will be used subsequently when the stability of the state of aggregation of the OMC are considered) and, on the other hand, such interactions can lead to steric hindrance to the formation of metal–ligand bonds. The first effect always increases the stability of the state of aggregation of OMC (see below), while the second reduces the stability of the OMC molecule.

The influence of non-bonding interactions (steric effects) on the molecular structure of the OMC and its stability has been noted in many communications (see, for example, Wilkinson[13] and Davidson et al[14]), but few systematic studies of this problem have been made, (see, for example, Refs.57–60).

There exist several methods for the quantitative estimation of the bulk of the substituents (ligands) and hence of the extent of non-bonding interactions in OMC molecules.[58–60] One of these, described by the present authors,[58] consists in calculating the solid angles formed by the substituents (ligands) with the vertex at the metal atom (Fig.1*a*). Cylindrical projections of the molecule can be usefully employed for such purposes in the molecules of polynuclear OMC containing chains of metal atoms.[58] It is possible to use the method proposed also for transition metal clusters. Fig.1*b* presents the dependence of the solid angles q on the M–X distance, where X is an atom of the substituent (ligand) linked to the metal atom M (for certain ligands). The sum of the solid angles for all the substituents (ligands) in the molecule

$$Q = \sum_{i=1}^{n} q_i,$$

where n is the number of substituents (ligands) in the molecule, can be used for the *a priori* estimation of the possible existence of molecules from the standpoint of steric hindrance due to non-bonding interactions, because this sum should be less than or equal to half the solid angle 4π. The quantity $Q > 4\pi$ indicates the possibility of steric hindrance and hence a low probability of formation or stability of the suggested OMC molecule. Conversely, the quantity $Q < 4\pi$ indicates the absence of steric hindrance to the formation of the molecule and at the same time characterises the degree of shielding of the metal atom in the latter by the substituents (ligands).

The energy and steric factors together determine the electronic and steric molecular structures of the OMC and their separation in merely methodological in character. Indeed,

the set of solutions of the Schrödinger equation with variation of the steric parameters (coordinates of the atoms or fragments of the OMC molecule) defines the potential energy surface (PES), describing all the states of the OMC molecule in terms of spatial coordinates. Equilibrium interatomic (interfragment) distances, which correspond to equilibrium between the forces of attraction and repulsion between the fragments of the molecule, correspond to the minimum on the PES (i.e. to a stable state of the OMC). Allowance for the non-bonding interactions of the non-bonded fragments of the OMC molecule in the calculation of the PES makes it possible to estimate the most favourable steric molecular structure of the OMC[61] and hence obtain an idea about the stability of the molecule.

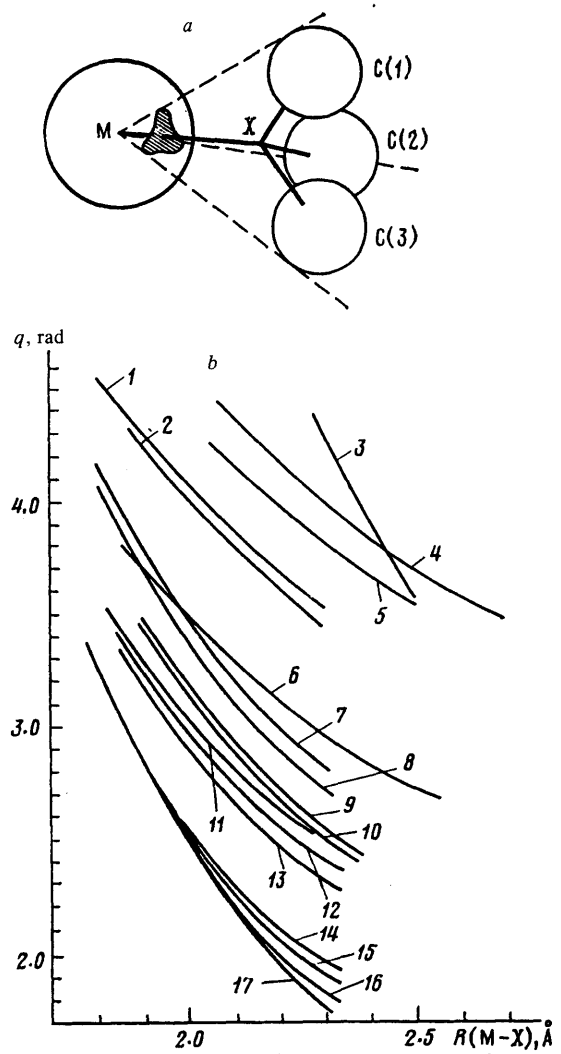


Figure 1. *a*) Scheme illustrating the structure of the solid angle *q* made by the substituent; *b*) dependence of the solid angle *q* on the distance R(M–X) for certain common substituents and ligands (an ideal tetrahedral or planar-trigonal coordination has been assumed for the atom X of the substituent).[58] Substituents: 1) CPh_3; 2) $CH(SiMe_3)_2$; 3) η^5-Cp; 4) $SiPh_3^F$; 5) $Si(t\text{-}Bu)_3$; 6) PPh_3; 7) CH_2CMe_3; 8) $2,4,6\text{-}Me_3C_6H_2$; 9) CH_2SiMe_3; 10) CF_2CF_3; 11) CCl_3; 12) CMe_3; 13) ferrocenyl; 14) η^1-Ph; 15) CF_3; 16) η^1-Cp; 17) Me, Et.

The stability of the electronic structure of the molecule on the PES is determined by the extent to which the transition of the electronic structure of the OMC from the surface corresponding to the ground electronic state to one corresponding to excited electronic states, including dissociative states, is hindered. Molecules, for which the intersection of the PES for the ground state with the PES for the excited states requires a considerable energy expenditure and deformation of the molecule (which is extremely probable for steep walls of the potential well on the PES of the OMC) apparently have stable electronic and molecular structures. In those cases where a potential well with sloping walls corresponds to the ground state of the OMC and, at the same time the PES for the ground state has no close intersections with the PES for the excited electronic states, the electronic structure of the OMC is stable and the molecular structure is labile relative to changes in the distances between the fragments.

We shall now consider the susceptibility of the OMC molecule to perturbations in the structure, which displace it from its position of stable equilibrium. The response of the OMC molecule to perturbation depends both on the type of the latter and on the nature of the bonds in the molecule. The following principal types of perturbations in the OMC molecular structure, characterising its stability, can be differentiated: (1) movement of a fragment and ligand forming part of the OMC molecule, which leads to homopolar bond dissociation with formation of neutral species; (2) movement of a fragment and ligand forming part of the OMC molecule leading to heteropolar bond dissociation with formation of charged species (ions) with opposite charges; (3) shifts of electron density and nuclei in the OMC molecule in opposite directions leading to the ionisation of the molecule to give the cation OMC^+ and an electron (characterised by the OMC ionisation potential and the redox potential in solution).

From general considerations, it is easy to conclude that the polarity of the metal–ligand bonds in the OMC as well as the bond energies play an important role in determining the ease of each of the three perturbation processes. A number of conclusions concerning the polarity of the bonds and the character of the MO in the OMC of non-transition and transition metals can be arrived at by assuming, in conformity with the Koopman's theorem,[40] that the one-electron MO may be responsible for the ionisation potentials of the molecule.[21]

A characteristic feature of non-transition metals whose ionisation potentials (IP_M) are of the order 4–8 eV is the reaction with organic radicals, whose ionisation potentials (IP_R) are about 8–10 eV, to form OMC which have $IP_{OMC} > IP_M$ (for $IP_R > IP_M$) in the absence of non-bonding electrons in the metal and a populated d^{10} shell in post-transition metals (Fig. 2*a*).[21] As a consequence of the electropositivity of the metal, the contribution of the substituent orbital to the populated bonding MO is higher than would correspond to the formation of a polar M–R bond with a negative charge on the substituent. For similar ionisation potentials $IP_M \cong IP_R$, the M–R bond is significantly non-polar (covalent), although $IP_{OMC} > IP_M \cong IP_R$. For metals and substituents for which $IP_M > IP_R$, the negative charge of the dipole of the M–R polar bond is localised at the metal atom and the bonding MO involves a predominant contribution by the atomic orbital of the metal.

For transition metals having $IP_M \cong 7$–8 eV combined with organic π–η^n-ligands, for which $IP_R = 8$–9 eV, the situation is somewhat altered. Since transition metals have *d* electrons and unfilled atomic orbitals, while the π–η^n-ligands have filled and unfilled MO, it follows that, together with covalent bonds, there is a possibility of the formation of both donor–acceptor and dative bonds (Fig. 2*b*).[21] The formation of donor–acceptor bonds, using the electron pairs of the ligands

and the AO of the metal, requires, as an essential condition, the rearrangement of the electron shell of the metal with liberation of the lowest AO having the appropriate symmetry and the filling, as a rule, of the d_δ and d_σ orbitals of the metals, among which the d_δ orbitals are involved in the formation of dative bonds with the antibonding MO of the ligands.

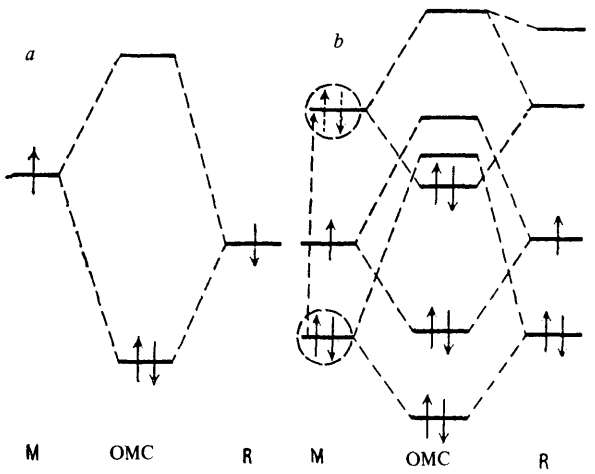


Figure 2. Molecular orbital diagrams for the OMC of non-transition (*a*) and transition (*b*) metals;[21] M = metal; R = substituent or ligand; the dashed arrow denotes the rearrangement of the electron shell.

In most cases the lowest bonding MO of the OMC molecule, corresponding to the donor–acceptor bonds, involve a large contribution by the ligand MO; MO with moderate energies, corresponding to covalent bonds, involve approximately equal contributions by the AO of the metal and the MO of the ligands, while the highest MO usually have the character of non-bonding or weakly bonding MO localised at the metal, since $IP_M \cong 7-8$ eV and the ionisation potential of the antibonding ligand MO is usually ~3–4 eV. Hence one can reach two conclusions. Firstly, since the formation of the optimum number of bonds ensuring the minimum energy of the OMC molecule requires a rearrangement of the ground electronic state of the transition metal to give an excited state, the upper electrons should be distributed in higher energy levels than the electrons of the free metal atom and should be non-bonding or weakly bonding in character. Secondly, the effective charge on the metal atom can be estimated from the energies of these non-bonding electrons. A survey of data for the IP_{OMC} of transitions metals[21,41] shows that $IP_{OMC} \leq IP_M$. This indicates an insignificant deviation of the charge on the metal from zero, which has in fact been confirmed by calculations yielding results close to the experimental data, for example, for ferrocene[62] and dibenzenechromium.[63–66] Thus, predominantly non-polar (covalent) bonds are observed in many η^n-derivatives of transition metals, with the exception of a number of compounds of the type of manganocene and cyclopentadienyl derivatives of the lanthanides, as a consequence of the mutual compensation of the shifts of electron density owing to donor-acceptor and dative interactions.

Having adopted the polarity of the metal–ligand (substituent) bond as the factor influencing the ease of both dissociation [homopolar (2) or heteropolar (3)] and ionisation processes, we shall now consider the characteristics of the energy relations of these processes.[66–73] If it is assumed that the OMC contains a polar $M^{\delta+}-R^{\delta-}$ bond, then its possible dissociation processes can be formulated as follows:

$$M^{\delta+}—R^{\delta-} \rightarrow M^0—R^0 \rightarrow M^0+R^0; \quad (2)$$

$$M^{\delta+}—R^{\delta-} \rightarrow F^+ + R^-. \quad (3)$$

Dissociation via scheme (2) should be accompanied by the abolition of the polar bond in the course of its dissociation.[20,21,66,73] Estimation of the energy of the displacement of the electron pair in the polar bond (the ionic component ΔE) by the method of Razuvaev et al[20] showed that different M–R bonds have different values of ΔE. Small, nearly zero values of ΔE are favourable for reaction (2), while higher values of ΔE hinder it.[20] Conversely, higher values of ΔE favour reaction (3) while low values hinder it. The ionisation process is promoted by low values of IP_{OMC} and also by high energies of the exciting quanta. The conditions associated with thermal reactions or multiquantum infrared excitation correspond to the first type of perturbation, which is milder and leads to homopolar dissociation. As a consequence of the greater strength of the more ionic bond, reaction (3) is promoted as a result of excitation by higher energy quanta (electron impact and ultraviolet, X-ray, and γ-ray quanta) or by the delocalisation of the separating charges on solvation and on exposure to an electric current in solution.[67–71]

III. THERMODYNAMIC STABILITY

The quantum-chemical stability of the OMC considered above determines the possibility, in principle, of the formation and existence of an isolated OMC molecule. If such a possibility exists, then the set of molecules forming a definite state of aggregation of the given substance can be stable in relation to any one decomposition process under some conditions, while under others it is unstable. The state of equilibrium in the thermodynamically reversible OMC $\rightleftarrows$ decomposition product system, the decomposition products involving different combinations of states of aggregation, is a measure of the thermodynamic stability of the OMC in relation to any decomposition process and is determined by the sign and magnitude of the change in the Gibbs free energy ΔG in this process.

The thermodynamic stability of coordination and organometallic compounds in relation to heteropolar dissociation into gaseous or solvated ions, i.e.

$$R_nM \rightleftarrows nR^- + M^{n+} \quad (4)$$

differs significantly from that for the homopolar dissociation into gaseous or solvated uncharges species (decomposition products):

$$R_nM \rightleftarrows nR + M. \quad (5)$$

Since reaction (4) in the gas phase involves charge separation, it is very greatly hindered by energy factors, i.e. it has high values of ΔH and is facilitated by solvation of the ions in solution. (There exists an extensive literature on the stability of coordination compounds in solution in relation

to reaction (4).[67-71] In view of the much lower values of ΔH, in the gas phase at temperatures up to ~1000° virtually the only dissociation process is the homopolar reaction (5).

Accordingly, the thermal stability, frequently discussed as a general characteristic of the OMC,[7,35,72] should be defined as the stability of OMC in relation to reaction (5) in all the aspects (quantum-chemical, etc.) discussed in this review. As a criterion of the thermal stability of OMC in its thermodynamic aspect, one must consider the presence of equilibrium in the homopolar bond dissociation process,[20,73] with formation of uncharged species: the metal and radicals (for ligands with an odd number of electrons involved in the formation of the bond) or molecules (for ligands with an even number of electrons participating in the formation of the bond). The reverse reaction in this case involves the synthesis of OMC from the decomposition products.

For a general consideration of the thermodynamic stability of OMC in thermal processes, we shall examine three main cases:

$$R_nM\ (gas) \rightleftarrows nR\ (gas) + M\ (gas), \quad (6)$$

$$R_nM\ (cond.) \rightleftarrows nR\ (cond.) + M\ (gas), \quad (7)$$

$$R_nM\ (gas) \rightleftarrows nR\ (gas) + M\ (solid), \quad (8)$$

where (gas), (cond.), and (solid) denote respectively the gas, condensed, and crystalline phases.

The homogeneous gas-phase process (6), under conditions where the states of the reactant obey the relations for ideal gases, is an analogue of the homopolar dissociation process (2), considered in its quantum-chemical aspect for the isolated states of the reactants. Because of this, the dissociation energies (D_n and $\bar{D}$) are identical with the dissociation enthalpy ΔH_D^0 for reaction (5). In describing the equilibrium in the decomposition reaction of polyatomic OMC molecules, one frequently employs the average enthalpy and entropy of dissociation of the metal–ligand bond. The results of the measurements of the energies and entropies of dissociation of the metal–organic ligand or radical bond have been discussed.[41-43,74-76]

Comparison of the enthalpy (ΔH) and entropy ($T\Delta S$) contributions to the Gibbs free energy (ΔG) of dissociation via reaction (6) for virtually all the known and investigated OMC[74] has shown that under standard conditions the contribution of the entropy term is only 5–30% of ΔH. Bearing in mind that the dissociation energies of all the bonds are positive[75] and that the entropy change on dissociation is likewise positive,[74] one may conclude that ΔG for all OMC dissociation processes in the gaseous state with formation of gaseous decomposition products and the metal vapour is always positive under standard conditions. Consequently almost all the OMC investigated hitherto are thermodynamically stable in relation to the gas-phase dissociation process at 298.15 K and a pressure of 1 atm. These conclusions confirm indirectly the results of extensive synthetic studies[24,25] during the last 10–15 years on the reactions of atomic (gaseous) metals with organic compounds when they are subjected to cocondensation at low temperatures.

With increase of temperature (at a constant pressure $p = 1$ atm), the contribution of the entropy term rises and at a specific temperature $T_{p,gas}$ the free energy ΔG of the dissociation reaction (6) becomes zero and then negative. Starting from this temperature, the OMC decomposition process becomes thermodynamically probable. The temperature $T_{p,gas}$ can be adopted as the temperature of the "onset" of the gas-phase OMC decomposition reaction characterising the thermal stability of the OMC in relation to the gas-phase decomposition reaction (6).

An estimate of the influence of pressure on the thermal stability of OMC has shown[21] that (1) at an elevated pressure the thermal thermodynamic stability of OMC is higher than at a reduced pressure; (2) the OMC thermal decomposition processes at a reduced pressure should occur at lower temperatures than at elevated pressures. These conclusions have been demonstrated qualitatively by known facts, namely that dibenzenetungsten(0) and dibenzenemolybdenum(0) decompose in a high vacuum at much lower temperatures than in a closed volume under the pressure of both decomposition products.[77,78]

Systematic studies have been made on the dependence of the dissociation energies[75] and dissociation entropies[74] of chemical bonds on the atomic numbers of the elements. It has been shown that the average dissociation energies $\bar{D}$ for compounds of non-transition elements within one Group in the Periodic System with carbon diminish with increase of the atomic number of the element, while for compounds of transition metals the opposite relation is observed: the average dissociation energy of the σ-bonds increases with increasing atomic number of the element down the Group.[75] This is also true of biscyclopentadienyl compounds, carbonyls, and other types of compounds of transition metals. On moving along the 3*d* series of transition metals, $\bar{D}$ diminishes with increasing atomic number of the element.[75,76] For the same non-transition element M in the analogous compounds, the values of D decrease in the following sequence as R is varied: Ar > Alk > Ph > Me > Et ≅ n-Pr ≅ n-Bu.[43]

The average M–C bond dissociation energies for non-transition elements reach a maximum on moving along the Period for Group IV elements.[43] The increase of $\bar{D}$(M–Alk) after the introduction of electron-accepting substituents into the OMC molecule, of the type $Alk_{n-m}MX_m$, where X = Cl, Br, I, or OH, compared with Alk_nM is of interest.[43] For the organobimetallic compounds $Alk_3M–MAlk_3$, the dissociation energies $\bar{D}$(M–Alk) are equal to those in Alk_4M; the metal–metal bond dissociation energies in compounds of the type $Alk_3M–MAlk_3$, which have been investigated, diminish in the sequence Si–Si > Ge–Ge > Sn–Sn,[43,76] while for the $M_{non\text{-}trans}–M_{trans}$ bonds [in compounds of the type $CpM_{trans}(CO)_3–M_{non\text{-}trans}Me_3$] the values of $\bar{D}$ lie in the sequence Cr–Ge < Cr–Sn < Mo–Ge < W–Ge < Mo–Sn < W–Sn, i.e. $\bar{D}$ increases with increasing atomic numbers of both metals, which is characteristic of transition metal OMC and not of non-transition metal OMC.

Analysis of the dependence of the average bond dissociation entropy on the position of the element in the Periodic System has shown[74,75] that $\Delta\bar{S}$(M–C) varies within much narrower limits than $\bar{D}$(M–C) and is in the range 15–45 cal mol^{-1} K^{-1}, the greatest number of values of $\Delta\bar{S}$ obtained lying in the range 30–40 cal mol^{-1} K^{-1}. Here $\Delta\bar{S}$(M–C) for the same Group of the Periodic System and isotypical compounds decreases with increasing atomic number, the effect being less pronounced for the heavier transition metals. The effect has been attributed[74,75] to the variation of the atomic radius of the metals in the Periodic System.

The $\Delta\bar{S}$(M–C) and $\bar{D}$(M–C) data can be used to calculate the average Gibbs free energies of dissociation of the bonds $\Delta\bar{G}$(M–C),[74] which may serve as a criterion of the stability of the OMC and the M–C bonds in them under standard conditions. The ΔG(M–C) for the OMC of non-transition and transition elements have been compared.[75,76]

Estimates of ΔG^0 [21,76,79] for the reactions

$$M\ (gas) + 2(C_5H_{5+n})\ (gas) \rightleftarrows (C_5H_5)_2M\ (gas) + nH_2\ (gas);$$

$$M{=}V,\ Cr,\ Mn,\ Fe,\ Co,\ Ni;\ n{=}0,\ 1,\ 3,\ 5.$$

$$Cr\ (gas) + 2(C_6H_6)\ (gas) \rightleftarrows (C_6H_6)_2Cr\ (gas).$$

show that the equilibrium in the gas-phase reactions with a

gaseous metal, involving synthesis and decomposition, is almost always displaced towards synthesis regardless of whether gas-phase radicals or stable organic compounds of the type of benzene or cyclopentadiene participate in the reaction. Although the entropy term contributes significantly to ΔG at elevated temperatues, the differences between the average M–C bond dissociation energies for different elements, the characteristic features of the variation of which were indicated above, should exhibit a marked influence.

On passing to heterogeneous OMC synthesis and decomposition processes (7) and (8), one should note the importance of considering the energy relations and the structures of the condensed phases of the reactants. If the condensed phase (crystal) has a molecular type of packing, then the contributions of ΔH and ΔS for the condensed phase of the OMC and the organic compounds, which occur in different parts of the reaction equation, partly cancel out and the position of the thermodynamic equilibrium in the synthesis-decomposition reaction involving the gaseous metal does not vary very markedly.[25,79] Specific features can be introduced only by intermolecular interactions in the condensed OMC phase additional to the van der Waals interactions. If the synthesis-decomposition reaction of the gaseous OMC with formation of gaseous organic decomposition products and the solid metal [Eqn.(8)] is considered, it is noted that the state of thermodynamic equilibrium in the reaction differs significantly from that for a purely gas-phase reaction. In the reaction involving the formation of the solid metal, for which this phase state is standard, the enthalpy of atomisation of the solid metal ΔH_f[M(gas)], i.e. the term which made a positive contribution to ΔG when the decomposition reaction was considered, giving rise to $\Delta G > 0$, virtually disappears and the state of equilibrium becomes markedly dependent on the enthalpy of formation of the decomposition products and on the entropy terms. Cases may be observed where $\Delta G > 0$ and $\Delta G < 0$, depending on ΔH_f[M)gas)] and other factors, for different OMC where the state of equilibrium of the gas-phase reaction is displaced towards synthesis.[21,25,79–81]

The radical change in the thermodynamic equilibrium and hence in the thermodynamic stability of OMC in the synthesis-decomposition reaction of dibenzenechromium(0) may be regarded as a classical example. While the equilibrium in the gas-phase reaction under standard conditions is displaced towards synthesis (see above), the equilibrium in the reaction involving the solid chromium phase is almost always displaced towards decomposition[21] under the same (standard) conditions:

$$(C_6H_6)_2Cr\ (gas) \rightleftarrows Cr\ (solid) + 2(C_6H_6)\ (gas).$$

Thus dibenzenechromium(0) is thermodynamically unstable in relation to the gas-phase decomposition with formation of solid metallic chromium. Such instability is manifested to an even greater extent for the bisarene derivatives of refractory metals, such as vanadium,[82] molybdenum,[77] tungsten,[78] titanium, niobium, and tantalum[83] as a consequence of the extremely high enthalpy of atomisation of the metals ΔH_f[M(gas)].

In the general case, for reactions involving the segregation of the solid metal, equilibrium should be attained at lower temperatures than for a purely gas-phase reaction.

For non-transition metals, for which the values of ΔH_f[M(gas)] are as a rule much lower, a shift of the equilibrium in the synthesis-decomposition reaction with participation of the solid metal towards synthesis is more likely,[80] as, for example, has been frequently observed for OMC of aluminium and certain other metals[81] and is also known from Paneth's classical studies on the reactions of free radicals with metallic mirrors.[15]

Thus the thermal thermodynamic stability of OMC is different for different decomposition reactions and is determined both by the thermodynamics of the OMC itself and by the phase state and the thermodynamic characteristics of the decomposition products.

In view of the foregoing, one may conclude that the thermodynamic stability of OMC in relation to the gas-phase decomposition process characterises, as it were, the possibility of the existence of the OMC in the gas phase (in the molecular form) and is thus close to the definition of the quantum-chemical stability, but refers solely to the set of OMC molecules in equilibrium with their decomposition products.

The thermodynamic stability of OMC in relation to the decomposition process with formation of the solid metal is more closely related to the definition of thermal stability in a real thermal decomposition process used to deposit coatings from the vapour phase and is more likely to characterise the reactivity of OMC than the possibility of the existence of OMC of the given type. The thermodynamic equilibrium between the solid metal and the gaseous OMC is attained more readily with increase of the surface area of the solid phase. It is noteworthy that the state of equilibrium for the solid metal and the condensed states of the OMC and the organic compound is likewise determined mainly by the high value of ΔH_f[M(gas)] and characterises the stability of the condensed state of the OMC in equilibrium with the solid metal. The majority of the OMC of refractory transition metals are thermodynamically unstable in these processes under standard conditions.[21,77–79,82] The thermodynamic instability of the OMC in relation to a specific decomposition process can be compensated by the kinetic stability and conversely, by virtue of the kinetic instability, in certain processes the thermodynamic stability may not be of decisive importance and the equilibrium (reversibility) of the process may be disturbed as a consequence of the operation of kinetic factors.

The transition from the gaseous to condensed (liquid or solid) states of the OMC is characterised by a significant change in the structure of the OMC. Apart from the molecular structure, the latter includes the relative disposition of the molecules, reflecting the intermolecular bonds (their packing).

Analogously to the way in which the molecular structure characterises the steric factor in electronic-nuclear interactions in the molecule, the structure of the condensed state of the OMC characterises the steric factor in the electronic-nuclear interactions in the set of molecules comprising the given states.

We shall consider the general types of the possible interactions between the OMC molecules in the condensed state: substituent (ligand)–substituent (ligand) (R ... R), substituent (ligand)–metal (R ... M), and metal–metal (M–M). The R ... R interactions are characteristic of organic chemistry, while the R ... M and M–M interactions constitute the specific features of the OMC.

The R ... R interactions are of the van der Waals type with energies up to 5 kcal mol^{-1}; their capacity for the formation of bonds is a maximum over a range of distances of ~2.5–3.5 Å.[84] These interactions determine the structure of molecular crystals.[84]

The intermolecular coordinate bonds with energies of ~3–10 kcal mol^{-1},[85] which lead to the formation of oligomeric and polymeric structures,[85–87] belong to the class of R ... M interactions. In the limit, these interactions can result in the formation of the R–M chemical bonds. This is confirmed, for example, by the oligomeric and polymeric structures of metal alkoxides or β-diketonates.[86]

The metal–metal interactions can also lead to the association of the molecules in the given state of aggregation. Thus many instances of the formation of infinite chains of OMC molecules and crystals with metal–metal bonds are known (see, for example, Ibers et al.[88]). The energy of these interactions is low compared with that of the M–M chemical bond (for example, the Rh–Rh bond energy is 18 kcal mol^{-1} [89]). The upper limit of the distances corresponding to the M–M chemical binding (~3–3.5 Å[88]) is comparable to the R ... R intermolecular contacts.

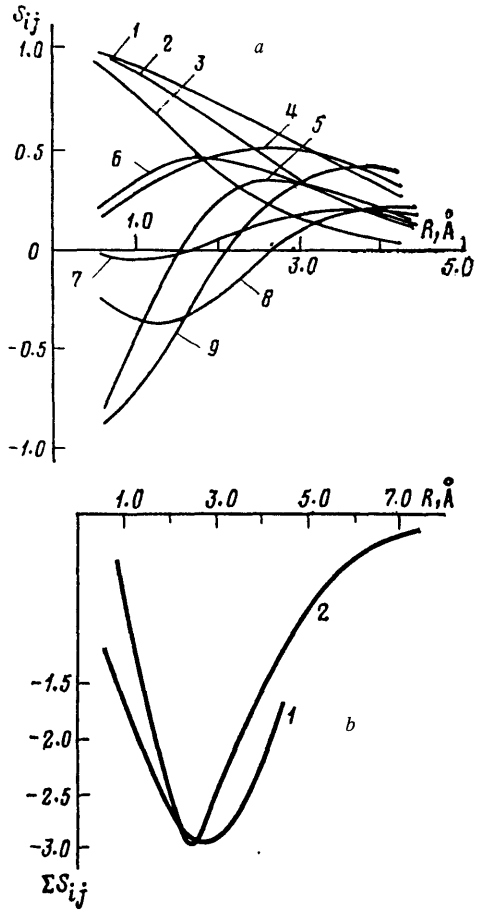


Figure 3. *a*) Dependence of the overlap integrals S_{ij} on the interatomic distance R in the Cr_2 molecule. The curves correspond to the following interactions: 1) 4*s*–4*s*; 2) $4p_\pi$–$4p_\pi$; 3) $3d_\sigma$–$3d_\sigma$; 4) 4*s*–4*p*; 5) $3d_\pi$–$3d_\pi$; 6) $3d_\pi$–$4p_\pi$; 7) $3d_\sigma$–4*s*; 8) $3d_\sigma$–$4p_\sigma$; 9) $4p_\sigma$–$4p_\sigma$; *b*) dependence of the sum ΣS_{ij} (curve *1*) and the potential of the Cr_2 molecule (curve *2*), calculated from experimental data in the form of the Morse potential, on the interatomic distance R in the Cr_2 molecule. Curves *1* and *2* have been normalised with respect to the minimum in curve *1*.

Analysis of the overlap integrals S_{ij} for the M–M bonds[90] has shown that for heavy metals the M–M interaction over distances of ~3–4 Å is still more intense and passes through a maximum for p_σ–p_σ, etc. Fig. 3 presents the values of S_{ij} based on the data of Batsanov and Zvyagina[90] and the semi-empirical Morse potential[91] for the Cr ... Cr interactions. In contrast to the "short range" Cr–C interaction, the Cr–Cr interactions are of the "long range" type and are characterised by a relatively broad minimum, which is due partly to a change in the contributions of different atomic orbitals of the metal.

All these factors confirm that it is legitimate to take into account the possibility of the formation of M–M bonds in considering the intermolecular interactions in OMC. The R ... R interactions have the character of boundary interactions and, in contrast to the R ... M and M–M interactions, are obligatory constituent elements of the intermolecular interactions in the condensed state of OMC.

On the basis of the foregoing, it is possible to trace the influence of the structure on the stability of the condensed state of OMC in relation to synthesis-decomposition processes, important for OMC and characteristic of such compounds, such as the formation of polynuclear OMC, metal clusters, and the solid metal from mononuclear OMC.

An estimate of the thermodynamic stability of the structure of the condensed state of OMC in relation to the formation in the latter of M–M bonds (apart from the intermolecular R ... R bonds) represents in essence an estimate of the stability of the structure of mononuclear OMC in relation to the formation of polynuclear OMC containing metal–metal bonds.

We shall estimate the contributions of the enthalpy and entropy terms to the ΔG of the transition from the structure of the OMC with intermolecular R ... R bonds to the structure with intermolecular R ... R and M–M bonds.

The enthalpy of the process consists of the changes in ΔH corresponding to the formation of M–M bonds and to the modification under these conditions of the intermolecular and intramolecular R ... R interactions. Overall, the intermolecular M–M interactions are energetically more favourable than the R ... R interactions. Consequently, in the absence of hindrance to the formation of M–M bonds by the R ... R interactions, the thermodynamic equilibrium is displaced towards the formation of the OMC structure with M–M bonds. The intermolecular (intramolecular) repulsion, which increases rapidly with decrease of the R...R distances, exerts the opposite influence and can render the formation of M–M bonds thermodynamically impossible.

The entropy term hinders the formation of M–M bonds, because the entropy of the system falls when they are formed ($\Delta S < 0$). ΔS depends directly on the steric hindrance to the formation of M–M bonds both by the molecular structure of the OMC and by the molecular packing: the greater the hindrance, the higher the value of ΔS.

Thus the structure of the condensed state of the OMC with intermolecular R...R bonds is more stable in relation to the OMC structure with intermolecular R...R and M–M bonds the greater the steric hindrance to the formation of these bonds by the intermolecular or intramolecular R...R interactions, in particular the higher the degree of shielding of the metal atom or the active centres in the substituents (ligands). Consequently, by creating a hindrance due to intramolecular and intermolecular non-bonding interactions, it is possible to achieve the stabilisation of the structure with R...R bonds relative to the formation of M–M bonds in the latter.

IV. KINETIC STABILITY

Since all real processes take place over a period of time, a significant factor determining the stability of OMC is the kinetics of the synthesis-decomposition reactions, the

principal features of which constitute the foundations of the concept of the kinetic stability and instability of OMC. Analogously to the previous two aspects of the consideration of the stability of OMC, the kinetic stability is determined for different processes involving perturbations in the state of equilibrium (the synthesis-decomposition of OMC). Under the conditions of the thermal processes (6)–(8), the kinetic stabiiity is one of the important components which determine the thermal stability of the OMC.

In order to determine the principal characteristics of the thermal kinetic stability of OMC, we shall consider the features of the gas-phase OMC synthesis-decomposition reaction:

$$R_nM \rightleftarrows R_{n-1}M + R \rightleftarrows R_{n-2}M + 2R \rightleftarrows \ldots \rightleftarrows M + nR.$$

Assuming that each of the consecutive stages presented above can determine the overall rate, consideration of the case where $n = 1$ or of the overall process

$$R_nM \rightleftarrows nR + M.$$

will not be an unduly drastic simplification. For $n = 1$, the process reduces to the dissociation reaction of diatomic molecules and the recombination of two atoms (or radicals), which have been thoroughly described in the literature.[92–95]

It is known from the theory of absolute reaction rates[96,97] that the intermediate activated state in the forward dissociation reaction and in the reverse recombination reaction is the same:

$$R{-}M \underset{k_2}{\overset{k_1}{\rightleftarrows}} [R{-}M]^{\neq} \rightleftarrows R + M.$$

However, the rates of the forward and reverse reactions can differ appreciably.

The forward dissociation reaction is a unimolecular process,[92] while the reverse reaction is a bimolecular process. The rate of the unimolecular dissociation reaction of RM may be determined by the rates of its two stages: (1) the activation process with formation of the intermediate activated state $[R{-}M]^{\neq}$ and (2) the transition of the activated state $[R{-}M]^{\neq}$ through the barrier with formation of the decomposition products.[96,97]

When equilibrium thermodynamics is used in the activated complex theory for the determination of the decomposition reaction rate constant, the latter is given by the following expression (the Arrhenius law):[92,93,96,97]

$$k = \varkappa \frac{kT}{h} e^{-\Delta G^{\neq}/RT} = \varkappa \frac{kT}{h} e^{\Delta S^{\neq}/R} \cdot e^{-\Delta H^{\neq}/RT},$$

where $\Delta G^{\neq}$, $\Delta S^{\neq}$, and $\Delta H^{\neq}$ are respectively the changes in the Gibbs free energy, entropy, and enthalpy of activation.

According to Moin,[98] $\Delta H^{\neq}$ is determined as the difference between the sums of the dissociation energies of the bonds being ruptured ΣD_r and the dissociation energies of the activated bonds $\Sigma D^{\neq}$:

$$\Delta H^{\neq} = \Sigma D_r - \Sigma D^{\neq}.$$

The factor kT/h characterises the frequencies of the collisions of the molecules during activation and increases with increase of temperature and pressure in gas-phase reactions.

The factor $e^{\Delta S^{\neq}/R}$ characterises the efficiency of the molecular collisions leading to reaction (the probability factor). The activation entropy $\Delta S^{\neq}$ then depends on the redistribution of energy between the different degrees of freedom in the activated state and is determined by the symmetry, i.e. by the steric structure of the OMC.

These kinetic features are valid both for the forward decomposition reaction and for the reverse synthesis reaction (recombination). The difference between the rates of the forward and reverse reactions is caused by the differences in the frequency and probability factors and in $\Delta H^{\neq}$. The kinetic conditions for the OMC thermal decomposition reactions and the reverse synthetic reactions have therefore proved to be such that the rate of one of the reactions is higher or lower than the other by any orders of magnitude.

The low overall OMC pressures *in vacuo* of the low OMC partial pressures in the carrier gas, used in carrying out the OMC thermal decomposition process, favour thermal decomposition at a higher rate and conversely they hinder the reverse synthetic reaction, which is significant only at high pressures, where the probabilities of binary and ternary collisions become appreciable.

Nevertheless the kinetic instability of OMC in the gas phase determined above is not decisive under the usual conditions at low temperatures where the rates of decomposition of OMC are low. Therefore, even in the presence of the solid metal, when the OMC may be thermodynamically unstable, as happens, for example, in the case of dibenzenechromium(0),[79] the OMC possesses kinetic stability as a consequence of the low rates of its decomposition; in other words, under these conditions the thermodynamic equilibrium is not established because of kinetic limitations. On the other hand, with increase of temperature the reaction rates also increase, which leads both to the rapid attainment of a state which is thermodynamically stable under the given conditions and to the manifestation of the kinetic instability of the OMC. These features can be clearly seen in relation to the synthesis-decomposition reactions of dibenzenechromium(0).[21,79]

Despite the thermodynamic stability of dibenzenechromium(0) in relation to the gas-phase decomposition reaction, it is kinetically unstable in the gas phase reaction because the forward decomposition reaction is a unimolecular process, while the synthetic reaction is a termolecular process or consists of two consecutive bimolecular processes, whose probability is low at reduced pressure compared with that of the unimolecular process. Since the rate of the forward gas-phase decomposition reaction of dibenzenechromium(0) should be much higher than the rate of the reverse synthetic reaction, an appreciable concentration of chromium atoms is established in the system. In view of the higher probability of a binary collision than a ternary collision, atomic chromium may recombine in binary collisions. If there is a possibility of removing the Cr–Cr bond energy to a third species or to the wall (support), the equilibrium in the recombination reaction shifts towards the formation of metallic clusters and ultimately of the solid metallic phase. Thus the kinetic conditions in the forward and reverse reactions may promote a shift of the reaction equilibrium to a thermodynamically unstable state—towards decomposition in the gas-phase reaction.

The appearance of the nuclei of metallic clusters and the solid phase during the process modifies the gas-phase reaction, so that the latter becomes a reaction with formation of the solid metal for which the fundamentally stable state is a dissociative state (decomposition).

Analysis of the conditions for the kinetic stability of gaseous substances and in particular of the OMC has shown that the stability increases with decrease of temperature and increase of pressure in the OMC $\rightleftarrows$ decomposition product system.[21]

From the standpoint of the influence of the structure on the kinetic stability of OMC, it is interesting to examine the effect of structure on the individual factors influencing the reaction rate constant. The factor kT/h is independent of the nature of the reactants and the activated state;[97] virtually the entire structural "load" is carried by the entropy (probability) factor $e^{\Delta S^{\neq}/R}$. If the structure of

the intermediate activated state differs little from that of the initial molecules, $\Delta S^{\neq}$ is low and the reaction rate falls. When the structure of the intermediate activated state of the complex is close to that of the decomposition products, $\Delta S^{\neq}$ is almost equal to the entropy of reaction ΔS and may be large and positive. If the intermediate activated state or the final products have a greater number of bonds than the initial reactants, $\Delta S^{\neq}$ may be negative, which diminishes the pre-exponential factor, although the formation of new bonds entails a decrease of the activation energy for the reaction (isokinetic law). Overall, the following statement may be made concerning the influence of structure on the entropy factor in the OMC thermal decomposition rate constant: the greater the rearrangement of the structure of the initial OMC in the intermediate activated state and the closer it is to that of the final products, the higher the decomposition reaction rate constant and the lower the kinetic stability of the OMC. Virtually no systematic estimates of $\Delta S^{\neq}$ for the OMC thermal decomposition reactions exist as yet; one can only point to a few investigations.[20,21]

The problem of the kinetic stability of OMC involves yet another important question, namely that of the efficiency of the activation energy transfer to the bond being ruptured, which depends on the distribution and the possibilities for the redistribution of the activation energy among the electronic, vibrational, and rotational degrees of freedom of the OMC molecule. The structure of the OMC may play a dual role in the redistribution of energy among the degrees of freedom and in its localisation in one of the stretching vibrations. If the OMC contain groups and fragments whose vibrations and rotations are of the type of symmetric or asymmetric tops, which interact strongly with other molecular vibrations, in particular, with the stretching vibrations responsible for the dissociation process, then in these molecules the activation energy is readily localised precisely in such torsional vibrations or rotations of the fragments and the probability of its localisation in the stretching vibration should be lower than in the molecules where such possibilities are absent.

Substituents and ligands of this type are, for example, the neopentyl (CH_2CMe_3), trimethylsilyl ($SiMe_3$), trimethylsilylmethyl (CH_2SiMe_3), benzyl (CH_2Ph), diphenylmethyl ($CHPh_2$), triphenylmethyl (CPh_3), adamantyl, cyclohexyl, norbornyl, cyanomethyl (CH_2CN), polychloromethyl ($CH_{3-n}Cl_n$), perfluoroalkyl (for example, CF_3), and other groups as well as ligands: $:C{\rightleftarrows}O$, $:PF_3$, and $:P(OR)_3$, where R = methyl, ethyl, phenyl, *o*-biphenylyl, etc.

Apart from their fairly high efficiency in delocalising the activation energy over the molecule, such substituents and ligands are able to shield the reaction centre, i.e. the metal–substituent (ligand) bond, from direct activation by virtue of their steric structure. The transmission of activation via the above groups to this bond is relatively ineffective as a consequence of the presence of a large number of high-energy vibrations in these fragments compared with the low-frequency stretching vibrations of the metal–substituent (ligand) bond and owing to the absence of the possibility of complex formation for the substituent. Such complex formation is possible for substituents of the type of allyl, alkynyl, and others as a consequence of a "viscous" ["non-elastic" (Editor of Translation)] collision with the multiple bond or collisions of substituted groups with hydroxy-, amino-, and other groups active in the formation of hydrogen bonds.

The steric shielding by the above substituents (ligands) of the central metal atom is such that the OMC molecule constitutes, as it were, an elastic sphere which is difficult to deform by compression and extension. Bearing in mind the chemical inertness of such substituents (ligands) in relation to both similar reagents and functional reagents, it is possible to account for the appreciable kinetic stability of OMC of this kind. A large number of kinetically stable OMC with substituents and ligands of the sort described have been obtained by Wilkinson and other workers.[13,14]

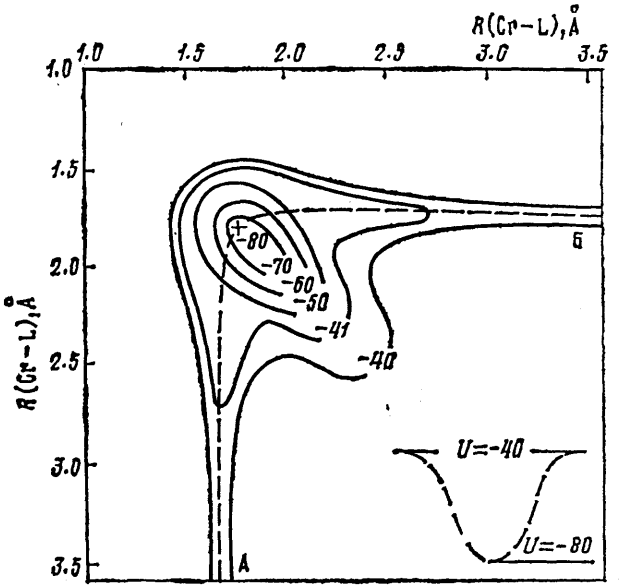


Figure 4. The potential energy surface for linear $(\eta^6\text{-L})_2Cr$ molecules, where L = C_6R_6 and R = H or Me.[61] States of the molecular fragments $(L^{(2)}\text{–Cr}\ldots L^{(1)}$ and $L^{(2)}\ldots\text{Cr–}L^{(1)})$ correspond to points A and B and the sign ± denotes the minimum in the potential well.

The set of energy and steric factors reflecting the kinetic stability or instability of OMC in a gas-phase process is in its turn reflected in the multidimensional potential energy surface for the OMC molecule. Fig. 4 illustrates the PES for dibenzenechromium(0),[61] which is characteristic also of other molecules of the type L_2M (L = ligand). The minimum in the potential well corresponds to a thermodynamically and kinetically stable state. Acquisition of an activation energy $E_a \geq D_1$ (D_1 is the energy of the abstraction of the first group L from the Cr atom) by the dibenzenechromium molecules induces movement along the reaction coordinate $Cr\text{–}L^{(1)}$ corresponding to the stepwise dissociation: $L^{(2)}\text{–Cr–}L^{(1)} \rightarrow L^{(2)}\text{–Cr} + L^{(1)}$. The activation energy in the unimolecular process is then virtually close to the dissociation energy D_1 of the first bond. Movement along the reaction coordinate $Cr\text{–}L^{(2)}$ arises similarly. After this, thermal activation takes place and the L–Cr fragment decomposes. For high levels of thermal excitation, following the absorption of light quanta or electron impact, there is a possibility of the transfer to the molecule of the energy $E_a \geq D_1 + D_2 = 2\bar{D}$. In this case there is a possibility of a concerted decomposition with the simultaneous dissociation of two ligands (movement

along the PES diagonal). This kind of decomposition of OMC is almost always observed when $D_2 < D_1$ and when $E_a \geq D_1$. The abstraction of a second ligand is greatly accelerated and takes place almost simultaneously with the first abstraction step (because $E_a \gg D_2$). A decomposition of this type has been observed for R_2Hg [99] and certain other OMC.

As in the consideration of the thermodynamic stability of OMC, we shall estimate the role of intramolecular and intermolecular non-bonding interactions in ensuring the kinetic stability of the condensed state of OMC relative to the formation of M–M bonds in the latter. The magnitude and sign of $\Delta H^{\neq}$ and hence also the rate of the process are determined by the relative contributions of opposite tendencies: the endeavour by the OMC to realise a state with M–M bonds (because this is favoured by thermodynamic factors) and the obstacle to this attempt by the M–R bonds and the non-bonding R...R interactions in the molecule and in the packing of the OMC.

The contribution of the entropy term retards the formation of M–M bonds, because the entropy change corresponding to this is negative. On the other hand, any change in the structure of the OMC involving a weakening and rupture of the M–R bonds is reflected in a positive contribution to $\Delta S^{\neq}$ (because the entropy then increases), which accelearates the process. Such structural changes are linked directly to the "rigidity" or "looseness" of both the molecular structure and of the packing of the OMC molecules. The more "rigid" molecules and molecular packing are kinetically more stable in relation to the formation of M–M bonds in the condensed state. The obstacles offered to the formation of M–M bonds in the condensed state of the OMC by the non-bonding R...R interactions and the "rigidity" or "looseness" of the structure are directly linked to the degree of steric shielding of the metal atoms from one another by the substituents (ligands), determined both by the molecular structure and by the molecular packing.

The symmetry (or, in other words, the degree of order) in the structure of the condensed state of the OMC plays an important role in such shielding. Since the character of the molecular collisions in the liquid (partial ordering) is such that their number is sufficient for the realisation of mutual orientations of the molecules which promote the formation of M–M bonds in the activated complex, one may conclude that in this case the steric hindrance to the formation of these bonds is generated mainly due to the shielding of the metal atom in the OMC molecular structure. In the crystalline state (total order) the possibility of the formation of M–M bonds is influenced also by the crystal packing. For example, the compound $(Ph_3Ge)_2Hg$ decomposes with liberation of metallic mercury in solution, on fusion, and also in the amorphous solid state, but is stable in the crystalline state, because the crystal packing of the molecules ensures the complete shielding of the Hg atoms from one another.[100]

Thus one may reach the following conclusion: the greater the steric shielding of the metal atoms from one another in the structure of the condensed state of the OMC (owing to its molecular structure or molecular packing), the more stable is this OMC state in the thermodynamic and kinetic aspect in relation to the formation of polynuclear OMC, metal clusters, and the solid metal, i.e. products containing metal–metal bonds.

The characteristic feature of the relation between the structure of the condensed state of the OMC and its stability in relation to the formation of M–M bonds described above is valid not only for mononuclear OMC of the type of MR_n but also for polynuclear OMC, namely metal clusters having the composition M_nR_m, because their molecules have in principle a structure analogous to that of the mononuclear OMC with the sole difference that in them not one atom but a group of metal atoms is surrounded by substituents (ligands). It is valid also for the characterisation of the stability of the condensed state of the OMC relative to the formation in the latter of intermolecular M...R bonds, i.e. the formation of oligomeric and polymeric structures.

V. THE STABILITY OF ORGANOMETALLIC COMPOUNDS UNDER NON-EQUILIBRIUM CONDITIONS

In most cases organometallic compounds exist in their synthetic and decomposition processes under the conditions of uncompensated energy (heat, radiation) and mass (changes in the relative amounts of the OMC and organic compounds—products resulting from decomposition and the segregation of the solid metal) fluxes. The presence of such fluxes disturbs the adiabatic conditions and leads to a non-equilibrium state of the system and to irreversible processes. Typical examples of such irreversible processes under non-equilibrium conditions include (1) the cryosynthesis of OMC with atomic (gaseous) metals,[24,25] (2) the deposition of the metal from the OMC vapour phase during thermal decomposition,[20,21] (3) the photodecomposition of OMC in the condensed or gaseous phase,[16,18] (4) the decomposition and synthesis of OMC under the influence of electron impact *in vacuo* or in a gas,[28,29] and a number of others.

The cryosynthesis of OMC with gaseous metals is an irreversible process by virtue of the very formulation of the experiment, because the latter employs extremely high supersaturations of the vapour phase with respect to the metal. The metal vapour obtained at high temperatures (~2000 to 2500 K) in a form in equilibrium with the condensed phase, is transported *in vacuo* as a flux of atoms which react at low temperatures with the condensed phase of the organic compound. At low temperatures the metal vapour is then in a state remote from equilibrium and the cryosynthesis of the OMC is therefore significantly irreversible.

The deposition of the metal from the vapour phase of the OMC during thermal decomposition[20,21] is carried out under the conditions of an energy (heat) flux through the support to the OMC and mass fluxes [of the OMC to the support and of organic compounds (decomposition products) from the support, condensed phase of the metal being deposited on the support]. The optimum conditions for the deposition process are then believed to be a flux of OMC unlimited with respect to time and an energy flux from the side of the support "unlimited with respect to power" and time.[20] Such conditions render the deposition process irreversible.

In the OMC decomposition processes under the influence of electromagnetic radiation (photodecomposition) or electron impact the distribution of the molecules with respect to energy differs from the equilibrium distribution and the decomposition products are frequently formed in electronically excited states[16,23,29] as a result of which these processes are likewise irreversible.

The kinetics of the irreversible processes under non-equilibrium conditions depend on how far the state of the system deviates from equilibrium. Near equilibrium, the rate of the process is usually linearly related to the process parameters and the method of stationary concentrations can be used for its description. Under conditions remote from thermodynamic equilibrium, non-linear relations are observed and are responsible for the presence of many different stationary states of the system and the occurrence of autowave processes and decaying vibrations in homogeneous gas-phase and liquid-phase reactions and in heterogeneous gas–solid and liquid solution–solid reactions.[101–106]

Apart from chemical kinetic factors, the study of non-equilibrium kinetics of irreversible processes[107] includes the consideration of mass-transfer (diffusion, turbulence) and heat transfer (thermal conductivity, convection) factors, small and large fluctuations in the state of the system, and also non-equilibrium states and irreversible processes in the interaction of the molecules with the electromagnetic radiation. The stability or instability of the system, in particular, of the OMC + decomposition products system, under such conditions, which approach those which obtain in reality, is determined by methods based on the theory of non-linear vibrations,[108] the non-equilibrium thermodynamics of irreversible processes,[101-104] synergistic relations,[109] or catastrophe theory.[106,110]

The OMC synthesis-decomposition processes occurring under conditions close to equilibrium should, generally speaking, lead to the decomposition of the structure,[101] while under conditions remote from equilibrium there is a possibility that the formation of dissipative structures may be observed. It is known[101] that chemical instabilities, which disturb the symmetry of the system, lead to the spontaneous self-organisation of spatial order in the system with formation of dissipative structures.[101-105]

The instability which leads to the disturbance of the symmetry in the arrangement of atoms or electrons is observed both in isolated molecules of OMC and coordination compounds (the Jahn–Teller effect[30]) and in solids (the charge-orbital ordering in the structure of the solid,[111] Peierls instability of M_n chains,[112] etc.).

The formation of metastable and high-temperature phases of the metal in the thermal decomposition of OMC,[21] the appearance of electronically excited states of the metal atoms and singly-charged metal ions on decomposition under electron impact (on the basis of emission spectra[29]) and on photo-decomposition or decomposition induced by a laser (on the basis of absorption[16] and emission[23] spectra), and the segregation of the metal under the conditions of the low-temperature decomposition of the OMC, in particular bistriphenylgermylmercury, on cooling the solution to 77 K[113] are evidence for the thermodynamic non-equilibrium state of the OMC + decomposition product system.

If the state of the OMC is thermodynamically stable (or chemically stable according to Gray[114]) and stable with respect to diffusion,[114] one can assume that such a state is stable as regards all aspects of stability (quantum-chemical, thermodynamic, kinetic, and macrokinetic) and is an equilibrium state. Chemical instability can never be observed in an equilibrium system but it can play an indirect role under conditions remote from equilibrium. The region of the phase space in which chemical instabilities can be observed is then always located near a region where diffusion instabilities exist.[114] The diffusion stability of an atomic metal + organic complex-forming compound system gives rise to the possibility, in the course of matrix synthesis, of the transition of the system to a kinetically and thermodynamically stable state of the OMC as a result of fluctuations. On the other hand, the diffusion instability of such a system leads to the thermodynamic instability of the OMC as a consequence of its kinetic instability, because of the possibility that the metal atoms may aggregate and an equilibrium may be established between the OMC and the solid metal or metal clusters having a large effective surface area.[25,80] Rigid or highly viscous matrices are therefore used for the synthesis of OMC with atomic metals. The breakdown of conditions for the matrix isolation of the metal atoms from one another and the diffusion instability of the matrix[24,115] lead to a greater probability of the formation of polynuclear OMC and metal clusters as products of the condensation of the intermediate compounds, in which the number of ligands at the metal is insufficient for the kinetic stabilisation of the OMC: $M + L \rightarrow ML \xrightarrow{ML} M_2L_2$ and $M + ML_2 \rightarrow M_2L_2$, etc. Reactions of bistoluenechromium(0) and bistoluenevanadium(0) of a similar type with chromium and vanadium atoms have been recently discovered.[116]

A good example of the formation of dissipative structures is provided by the irreversible heterogeneous gas–solid reactions used for the deposition of inorganic coatings from the vapour phase in the thermal decomposition of OMC.[20,21] The growing surface of the solid phase can be regarded as an open thermodynamic system in deposition processes.[117] The characteristic features of the formation of dissipative structures in these processes have been investigated in fair detail in a number of studies.[20,21,117-123] It has been shown that processes involving the formation of a solid phase (the attainment of stationary surface areas of the growing solid phase, the multiphase nature of the deposit, the aggregation of particles and their dynamic characteristics, and the layer structure of the particles formed in the kinetic region of the reaction),[117] OMC adsorption processes and processes involving the desorption of the decomposition products,[21] the possible autocatalytic processes,[118] the finite rate of removal of the decomposition products,[120] the limited thermal conductivity of the support, and the inadequate power of the heat flux through the support[121] play an important role in their formation. Vibrational and monotonic processes involving the attainment of stationary states,[119] the limitation of the rate of the deposition process with respect to pressure and the occurrence of a peak in this rate,[119] temperature hysteresis and the excitation of auto-oscillations in the rate of deposition,[121] the fixation of time oscillations in concentration and temperature in the form of three-dimensional layer structures of the coatings,[119,122,123] and also the fixation of three-dimensional fluctuations of the rate of growth in the form of columnar structures[21,123,124] and filamental crystals[21,125] have been observed experimentally. Studies of theoretical models of the deposition process have demonstrated their satisfactory agreement with experiment.[21]

The formation of dissipative structures in a solution of an OMC has been observed for allylpalladium compounds[126] under the conditions of hindered diffusion in Liesegang rings and also for the ferrocene–ferrocenium system on irradiation with visible light of their solutions in alcohols.[127]

Under the conditions of non-linear kinetics, there is a possibility of a state of the system such that the OMC decomposition process is strongly retarded, despite the existence of conditions under which the OMC might have been unstable both thermodynamically (according to equilibrium thermodynamics) and kinetically. In such cases the non-equilibrium thermodynamic stability of the OMC in relation to the decomposition process arises, but this stability corresponds to the attainment by the system of a stationary state which in the general case may be unstable in time (in relation to local structural fluctuations). This state may be called a dynamically stable non-equilibrium state, which corresponds to a definite degree of the thermal decomposition process.

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Thus one may conclude that a complex and varied problem such as that of the stability of OMC in their synthetic and decomposition processes must be solved only by a combined procedure on the basis of general concepts of the stability and structure of material systems taking into account all its aspects and the energy and steric factors. This approach makes it possible to investigate the stability of various types of OMC in relation to perturbations of any type, to reduce to

an integral unique system the results obtained in this field, and to discover various aspects of the problem and their interrelation. The approach can also help to abolish the existing confusion among investigators who mix up various aspects of the stability of OMC. On the other hand, the combined approach is very fruitful, because it allows one to use for the solution of the problem the advances in various sciences—chemistry, physics, and mathematics. It must be emphasised that the approach described permits the investigation of the OMC synthesis-decomposition processes, starting with idealised processes in an isolated OMC molecule and continuing up to real processes, which constitute the basis of a series of new promising technologies involving the industrial application of OMC.[20,21,24,25]

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